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 TI Lithographic plates and printing method
 IN Azuma, Kensaku; Yano, Haruhiko; Saeki, Shuji
 PA Tomoe-gawa Paper Mfg. Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 5 pp.
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CLASS

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AB The method uses lithog. plates having a recording layer containing blocked isocyanate and polymers that have active H reactive with isocyanates with the support and/or the recording layer containing an agent for light-to-heat conversion. The method consists of imagewise exposure of the material to high-energy radiation and removing the unirradiated part of the layer by washing. The material and method provide simple means of platemaking and good printability of the plates. Thus, a blocked isocyanate prepared from 2-methylimidazole and 1,6-hexamethylenediisocyanate was dispersed in EtOH. A composition containing 20% solution of isobutylene-maleic acid copolymer

100, 30% dispersion of the blocked isocyanate 35, and 50% dispersion of C black 2 g was applied on an Al-coated polyester film (3.5 g/m²). The plate was imagewise exposed to Ar laser and developed with EtOH. The use of the plate for printing gave 5000 clean prints, without damage to the plate.

ST lithog plate laser platemaking; laser lithog platemaking heat mode; isocyanate blocked photosensitive lithog plate

IT Lithographic plates
 (photosensitive, laser heat-mode)

IT 693-98-1D, 2-Methylimidazole, reaction products with isocyanates
 822-06-0D, 1,6-Hexamethylene diisocyanate, reaction product with
 2-methylimidazole 24936-97-8D, reaction products with TDI and
 methylimidazole 26426-80-2, Isobutylene-maleic anhydride copolymer
 77466-24-1

RL: USES (Uses)

(laser heat-mode lithog. plates containing)

RN 693-98-1D
 RN 822-06-0D
 RN 24936-97-8D
 RN 26426-80-2
 RN 77466-24-1

L8 ANSWER 2 OF 3 WPIX COPYRIGHT 2008
 AN 1987-239840 [34] WPIX
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THE THOMSON CORP on STN

TI Raw plate for lithographic printing - comprises base support with hydrophilic surface; recording layer; and photo-thermal energy conversion substance

DC A25; A89; G07; P74; P75; P84

IN AZUMA K; SAEKI S; YANO H

PA (TOMO-C) TOMOEGAWA PAPER MFG CO LTD

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AB JP 62164049 A UPAB: 20050819

The raw plate comprises a base support having hydrophilic surface, a recording layer containing blocked isocyanate and polymer having active H reactive with isocyanate, which is provided on the surface of the base support, and photo-thermal energy conversion substance contained in either base support or recording layer.

ADVANTAGE - The plate can be prepared by patterning with simple exposure to laser light, and simple development. - In an example, the raw plate was prepared by coating Al vacuum evaporated 125 micron polyester film with a compsn. comprising ethanol solution of isobutylene-maleic anhydride copolymer (solid content-20%) 100g, dispersion of blocked isocyanate in ethanol, which is synthesised from 2-methylimidazole 125g and 1,6-hexamethylene diisocyanate 125g, (solid content = 30%) 35g and dispersion of C black in ethanol (solid content = 50%) 2g. The lithographic plate was prepared by irradiating dried layer of the raw plate with Ar laser (wavelength = 4,880 angstroms, output = 1W, scanning speed = 2m/sec, line density = 15 lines/mm), and then washing out non-irradiated part with ethanol.

MC CPI: A08-C09; A08-D04A; A10-E24; A12-L02B1; A12-W07B; G05-A01; G06-D02; G06-D05; G06-F03C; G06-G17; G06-G18

L8 ANSWER 3 OF 3 JAPIO (C) 2008 JPO on STN

AN 1987-164049 JAPIO

TI LITHOGRAPHING PLATE MATERIAL AND PLATE MAKING METHOD

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PA TOMOEGAWA PAPER CO LTD

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PRAI JP 1986-5060 19860116

SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1987

IC ICM G03F007-02

ICS B41N001-14

AB PURPOSE: To enable easy plate making and to improve its printing characteristics by incorporating block isocyanate in a recording layer. CONSTITUTION: The recording layer containing the block isocyanate and a polymer having active hydrogen atoms capable of reacting with the isocyanate is formed on the hydrophilic surface of a base plate, and a substance capable of converting light into heat is added to at least either the base or the recording layer. It is imagewise exposed to high energy light to heat the recording layer through said substance and to form hydrophilic image parts, and then, the nonheated parts of the heat sensitive recording layer is washed and removed, thus permitting plate making to be easily executed only by a simple light irradiation means, such as means for irradiating laser beams, without requiring an expensive complicated plate making device, and its printing characteristics are improved.

PTO 08-2746

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PLANOGRAPHIC PRINTING ORIGINAL PLATE
AND ITS PLATE-MAKING METHOD
[Heiban Insatsu Genban Oyobi Sono Seiban Hoho]

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Specification

1. Title of the invention

Planographic Printing Original Plate and Its Plate-Making Method

2. Claims

1. A planographic printing original plate, characterized by the fact that a recording layer containing a polymer having an active hydrogen that can react with block isocyanate and isocyanate is installed on the surface of a substrate having a hydrophilic surface; and a photothermal converting substance is included in at least one of the substrate and the recording layer.

2. A method for manufacturing a planographic printing original plate, characterized by the fact that a planographic printing original plate, in which a recording layer containing a polymer having an active hydrogen that can react with block isocyanate and isocyanate is installed on the surface and a photothermal converting substance is included in at least one of the substrate and the recording

¹ Numbers in the margin indicate pagination in the foreign text.

layer, is irradiated in an image shape by a high-energy light; a lipophilic image part is formed by heating the recording layer through a photothermal conversion; and the recording layer of the unheated part is removed by washing.

3. Detailed explanation of the invention

(Industrial application field)

The present invention pertains to a new planographic original plate that can manufacture a plate by utilizing a high-energy light and a simple plate-making method using it.

(Prior art)

As a planographic printing plate, PS plate using a photosensitizer, electrophotographic master using zinc oxide, etc., are used. However, there were several drawbacks in these printing plate and plate-making method.

For example, since the PS plate is photosensitive, a sufficient caution is required for storing and handling for using. Also, in the plate-making, a pattern cannot be directly printed on a printing plate from an original, and a lithographic film is used as an intermediate medium. The process for processing the lithographic film is complicated, there are contaminative chemicals among the products being used, and there are problems in terms of

handling. On the other hand, in an electrophotographic method, plate-making is easy, compared with the PS plate, however an inexpensive apparatus of an electrophotographic plate-making machine is required. Thus, it cannot always be said that the electrophotographic method is a simple plate-making method. /2

(Problems to be solved by the invention)

The present invention considers the above-mentioned situation and provides a new planographic printing original plate and its plate-making method having simple plate-making operation and process.

(Means to solve the problems)

The present invention provides a planographic printing original plate characterized by the fact that a recording layer containing a polymer having an active hydrogen that can react with block isocyanate and isocyanate is installed on the surface of a substrate having a hydrophilic surface; and a photothermal converting substance is included in at least one of the substrate and the recording layer.

Also, the present invention provides a method for manufacturing a planographic printing original plate characterized by the fact that a planographic printing original plate is irradiated in an image shape by a high-energy light; a lipophilic image part is formed by heating

the recording layer through a photothermal conversion; and the recording layer of the unheated part is removed by washing.

The largest characteristic of the present invention is that a block isocyanate is mixed in a recording layer. The block isocyanate in the present invention can be obtained by putting the following isocyanate compound and a blocking agent at a prescribed mixture ratio into a reactor and heating. In this case, if necessary, a solvent and a catalyst for accelerating the reaction can be used.

In other words, the isocyanate compound is a curing agent of an epoxy resin and a polyester resin, and well-known compounds can be applied to the present invention. For example, alkylene diisocyanate such as 1,6-hexamethylene diisocyanate, 1,8-octamethylene diisocyanate, and 2,2,4-trimethylhexamethylene diisocyanate, unsaturated isocyanate such as 3,3'-diisocyanate dipropyl ether, 3-isocyanate methyl-3,5,5-trimethylcyclohexyl isocyanate, and trans vinylene diisocyanate, aromatic isocyanate such as toluene diisocyanate, xylene diisocyanate, 4,4'-diphenylmethane diisocyanate, phenyl isocyanate, and 4,4'-biphenyl diisocyanate, and prepolymer having isocyanate at the terminal are mentioned, however the isocyanate compound is not limited to these compounds.

On the other hand, as the blocking agent of the above-mentioned isocyanate, compounds such as phenol group, alcohol group, active methylene group, mercaptan group, acid amide group, imide group, amine group, guanidine group, imidazole group, urea group, carbamate group, imine group, oxime group, and sulfite group can be used.

The blocking agents especially suitable for synthesizing the block isocyanate in the present invention are phenol group, alcohol group, amine group, guanidine group, imidazole group, and urea group compounds. Specifically, as the phenol group, phenol, cresol, xyleneol, p-ethylphenol, o-isopropylphenol, p-tert-butylphenol, p-tert-octylphenol, thymol, p-naphthol, p-nitrophenol, p-chlorophenol, etc., are mentioned, and as the alcohol group, methanol, ethanol, propanol, butanol, ethylene glycol, methyl cellosolve, butyl cellosolve, methyl carbitol, benzyl alcohol, phenyl cellosolve, furfuryl alcohol, cyclohexanol, etc., are mentioned. Also, as the amine group, diphenylamine, phenylnaphthylamine, aniline, carbazole, etc., are mentioned, and as the guanidine group, guanidine, methylguanidine, 1,3-dimethylguanidine, acetylguanidine, phenylguanidine, 1,3-diphenylguanidine, 1,3-di-o-tolylguanidine, 1-dimethyl-3-methoxyphenylguanidine, 1-benzoyl-3-phenylguanidine, and o-

tolybiguanide are mentioned. As the imidazole group, imidazole, 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, and 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine are mentioned, and as the urea group, urea, thiourea, ethyleneurea, phenylurea, /3 etc., are mentioned.

In the present invention, along with the block isocyanate, as the polymer constituting the heat-sensitive layer, a polymer having an active hydrogen that can be cured by reacting with isocyanate being generated from the block isocyanate when heating is used. The isocyanate reacts with many functional groups, and in the present invention, a polymer having at least one kind of functional group being selected from a hydroxyl group and a carboxylic group is preferably used. As the polymer containing a hydroxyl group, a polyol prepolymer for a polyurethane resin such as polyether polyol, polyester polyol, acryl polyol, and epoxy polyol is mentioned. Also, as the polymer containing a carboxylic acid group, isobutylene-maleic anhydride copolymer, acrylic acid copolymer, methacrylic acid copolymer, etc., are mentioned. In

addition, a polymer containing an imino group or amino group such as ethyleneimine copolymer can also be used.

In the present invention, various kinds of catalysts can be included in the heat-sensitive layer to accelerate the isocyanate dissociation when heating the above-mentioned block isocyanate and to accelerate the curing reaction of the isocyanate and the polymer containing an active hydrogen. As its detailed examples, triethylamine, triethylenediamine, tin octoate, dibutyl tin di(2-ethylhexoate), lead 2-ethylhexoate, bismuth nitrate, titanate acid, 2-ethylhexyl, bismuth nitrate, tin (II) chloride, iron (II) chloride, zinc naphthenate, antimony trioxide, etc., are mentioned.

The photothermal converting substance being used in the present invention absorbs a high-energy light and converts the optical energy into a heat, and various kinds of coloring pigments and dyes are used. As its detailed examples, carbon black, cadmium oxide, sulfur, zinc oxide, cadmium sulfoselenide, sulfur, molybdenum red, iron oxide red, phthalocyanine blue, crystal violet, methylene blue, erythrosine, etc., are mentioned. In the present invention, these photothermal converting substances can also be mixed as a photothermal converting layer onto the

recording layer in addition to the mixture into the recording layer or substrate.

In the recording layer of the present invention, in order to raise the ink acceptability of the heating part, inorganic pigment such as calcium carbonate, silica, and aluminum hydroxide, organic pigment such as crosslinking styrene particulates, urea-formalin resin particulates, and benzoguanamine resin particulates, and waxy substances such as amide stearate, methylol stearamide, paraffin wax, microcrystalline wax, and montanic acid wax, and higher alcohol can be added. Also, if a heat-sensitive coloring material is added to the recording layer, whether or not recording is finished can be easily discriminated. As the coloring material, conventional well-known materials such as leuco dye, phenol compound, transition metal salt, and chelating agent can be used.

As the substrate having a hydrophilic surface in the present invention, metal plate such as desensitized aluminum plate and zinc, paper, resin-impregnated paper, and plastic film on which a desensitized metal foil is laminated or a metal such as aluminum is vapor-deposited are used. Also, a paper or plastic film on which a hydrophilic fine powder such as kaolin clay or silica is

spread along with a hydrophilic binder such as starch and a crosslinking agent of said binder can be used.

The recording layer is mixed with a dispersed solution or solution of a block isocyanate, a polymer solution containing an active hydrogen, a photothermal converting substance, and if necessary, various kinds of additive, spread on the hydrophilic surface of the substrate by wire bar, etc., and dried at relatively low temperature.

The planographic printing original plate of the present invention manufactured as mentioned above is passed through the following plate-making process and provided as a plate for planographic printing such as offset printing.

In other words, first, a high-energy light is irradiated in an image shape to the surface of the planographic printing original plate of the present invention. In this case, as a light source, various kinds of laser beams, xenon flash lamp, magnesium flash lamp, halogen lamp, infrared lamp, etc., can be used.

As a method for irradiating laser beams, many methods are well known, and in the present invention, for example, the light and shade of an original is converted into the 1/4 size of an electric signal by scanning a laser beam, and the laser beam whose intensity is modulated in accordance

with the size of the electric signal is irradiated onto the printing original plate.

In case a flash light is irradiated, a pattern to which a light transmittance is rendered in an image shape is adhered onto the printing original plate, and the flash light is irradiated from the pattern side.

The image part formed as a light-irradiated part as mentioned above is photothermally converted by the existence of a photothermal converting substance and heated. As a result, the isocyanate is dissociated from the block isocyanate of the image part and reacted with the active hydrogen such as hydroxyl group or carboxyl group of the polymer coexisting in the recording layer, so that the polymer is cured and made lipophilic. Thereby, an ink acceptability is provided during the planographic printing. Then, the unheated part, that is, the recording part of the uncured non-image part is removed by washing with water or a solvent, and the hydrophilic, that is, ink-nonadhesive substrate surface is exposed, so that the plate-making is completed. The solvent being used in the washing easily dissolves only the recording layer of the unheated part, and a paint solvent of said recording layer is appropriate. Specifically, alcohol, acetone, MEK, ethyl acetate,

isobutyl acetate, toluene, these mixed solvent can be used.

Also, an acidic water or alkaline water can be used.

After the washing process, if the mechanical strength of the image part or the adhesive strength with the substrate is deficient, curing of the image part can be advanced by further heating the entire surface.

(Application examples)

Next, the preparation of the planographic printing original plate of the present invention and the plate-making method using it are explained by application examples, however the present invention is not limited to them.

Synthesis Example 1

125 g 2-methylimidazole and 125 g 1,6-hexamethylene diisocyanate were charged into a three-necked flask with stirrer, thermometer, and cooler, and the reaction temperature was raised from the room temperature up to 75°C. Then, the reaction was carried out until a free isocyanate was not confirmed, so that a block isocyanate was obtained.

Synthesis Example 2

While dropping 35 g toluene isocyanate into 100 g butyl adipate (an average molecular weight of 1,000), a prepolymer of isocyanates at both terminals was obtained by reacting. 16 g 2-methylimidazole was added to the

prepolymer and heated at 105°C for 2 h, so that a block isocyanate was obtained.

Application Example 1

A recording layer paint with the following prescription was coated on an aluminum vapor-deposited surface of a substrate in which aluminum was vapor-deposited on a polyester film with a thickness of 125 μm by a wire bar and dried with warm air at 70°C, so that a planographic original plate having a recording layer spread at an amount of 3.5 g/m^2 was obtained.

Ethanol solution (20% solid fraction) of isobutylene-maleic anhydride copolymer	100 g
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Ethanol dispersed solution of the block isocyanate synthesized in Synthesis Example 1 (30% solid fraction)	35 g
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Ethanol dispersed solution of carbon black (50% solid fraction)	2 g
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Recording was carried out on the recording layer of this original plate under the conditions of a horizontal scanning rate of 2 m/sec and a line density of 15 pieces/mm by using an argon laser with a wavelength of 4,880 Å and an output of 1 W. Then, the non-irradiated part of the laser beam was removed by washing with ethanol.

This printing plate was set in a small-scale offset printer (Ryobi 2700 type), and 5,000 sheets were printed under ordinary printing conditions, so that printed matters with excellent sharpness were obtained without ground stains of the non-image part, separation of the image part, and wear of the plate surface.

Application Example 2

An aluminum vapor-deposited layer of 0.1 μm was installed on a polyester film with a thickness of 125 μm . A recording layer paint with the following prescription was coated on the aluminum layer by a wire bar and dried with warm air at 70°C, so that a planographic original plate having a recording layer spread at an amount of 3.0 g/m² was obtained.

Acryl polyol (made by Mitsui Toatsu Chemicals, Inc.:

Olester 0164, 45% solid fraction, solvent

toluene/MIBK-7/3) 30 g

MEK solution of the block isocyanate synthesized in

Synthesis Example 2 (20% solid fraction) 25 g /5

Ethanol dispersed solution of carbon black (50% solid fraction) 1 g

Toluene 10 g

MIBK 15 g

A pattern in which an aluminum plate was cut out was adhered onto the recording layer of this original plate and flash-exposed from the pattern side by a recording scale T-10 using Zenofax FX-150 made by Riso Kagaku Kogyo K.K. Then, this original plate was washed with a mixed solvent of toluene/MIBK = 1/1. Furthermore, this plate was heat-treated for 5 min by a dryer at 100°C.

When this printing plate was similarly printed, similar excellent effect could be obtained.
(Effects of the invention)

Since the present invention has the above-mentioned constitution, an expensive complicated plate-making apparatus is not required, unlike the conventional planographic printing plate, and a simple plate-making is realized only by a simple light irradiation means such as irradiation of laser beams. At the same time, its printing characteristics are also excellent.